(12) UK Patent Application (19) GB (11) 2 250 020 (13) A

(43) Date of A publication 27.05.1992

(21) Application No 9025667.8

(22) Date of filing 26.11.1990

(71) Applicant
Tioxide Group Services Limited

(Incorporated in the United Kingdom)

Tioxide House, 137–143 Hammersmith Road, London, W14 0QL, United Kingdom

(72) Inventor
Trevor Solomon

(74) Agent and/or Address for Service
John Wilkinson
Tioxide Group Services Limited, Central Laboratories, Portrack Lane, Stockton on Tees, Cleveland, TS18 2NQ, United Kingdom

(51) INT CL[5]
C09C 3/10

(52) UK CL (Edition K)
C1A AD1 AD41 AE3HC AE3HF AG10 AG13 AG24 AG33 AG39 AG4 AG4D10 AG4D28 AG4D45 AG40 AG46 AG47 AG48 AN30 AN34 AN36 AN4 AVF1 A302 A303 A304 A305 A307 A308
C3P PJR
C3W W209 W225 W227

(56) Documents cited
GB 2227739 A **HU 0035709 A**

(58) Field of search
UK CL (Edition K) **C1A AVF1 AVF3**
INT CL[5] **C09C**
Online databases: WPI AND CLAIMS

(54) Preparing pigments by coating inorganic particles with monomers polymerised in the presence of a dye

(57) Coloured inorganic pigments are prepared by a process in which particles of inorganic powders are coated with a polymer containing a dye whereby an ethylenically unsaturated monomer is polymerised in the presence of a dye and a dispersed inorganic powder having a cationic charge on the surface of the particles thereof.

The process is generally carried out as an aqueous emulsion polymerisation and preferred monomers are unsaturated carboxylic acids or esters. Preferably the inorganic powder is titanium dioxide.

The process provides a pigment which is readily dispersed in organic media and which provides a primary opacifying effect due to the inorganic powder combined with a colouring effect due to the dye.

GB 2 250 020 A

The claims were filed later than the filing date within the period prescribed by Rule 25(1) of the Patents Rules 1990.

INFORMAL SPECIFICATION

PROCESS FOR PREPARING PIGMENTS

This invention relates to a process for the preparation of pigments and particularly to a process for the preparation of coloured inorganic pigments.

According to the present invention a process for the preparation of coloured inorganic pigments comprises polymerising a reaction mixture of an ethylenically unsaturated monomer in the presence of a dye and of a dispersed inorganic powder having a cationic charge on the surface of the particles thereof, said monomer being present in an amount not greater than 200% of the weight of said powder so that said particles are coated with polymerised monomer containing said dye.

The process of the invention provides a pigment which is readily dispersible in organic media and which provides a primary opacifying effect due to the inorganic powder combined with a colouring effect due to the dye. This combination can yield more uniformly pigmented systems than the use of the inorganic powder and the dye as separate components. The process also provides an efficient means by which virtually all the polymerised monomer is deposited on the inorganic powder particles and a minimum of free polymer is produced.

Generally speaking the process involves the preparation, initially, of a dispersion, usually an aqueous dispersion, of the inorganic powder to be coated, and, if necessary, the modification of the particles thereof so that the surface thereof carries a cationic charge. An ethylenically unsaturated monomer and a dye usually are

then added to the dispersion of the inorganic powder and polymerisation is initiated by an appropriate technique.

The dye may be added separately but simultaneously with the monomer but preferably the dye and the ethylenically unsaturated monomer are premixed before addition to the dispersion of inorganic powder. The dye may also be added at any time during the course of the polymerisation and may be present during only part of the polymerisation process so that only part of the polymer coating produced contains the dye.

In order to minimise the production of free polymer the amount of the monomer should not exceed 200 per cent by weight of the inorganic powder.

The process of the present invention can be used to coat the particles of any inorganic powder but those of more interest are the inorganic pigments, extenders and fillers. Particularly, inorganic pigments are found to be of most use in the process and such pigments are titanium dioxide pigments, aluminium oxide pigments, antimony oxides, barium pigments, calcium pigments, zirconium pigments, chromium pigments, iron pigments and magnesium pigments. Extenders and/or fillers such as silica, silicates, aluminates and particularly the clays can also be treated by the process of the invention. Mixtures of pigments and extenders can also be treated as well as non-pigmentary forms of the inorganic powders mentioned as pigments. In the most preferred process the inorganic powder is titanium dioxide pigment, preferably rutile titanium dioxide.

Desirably the inorganic powder is in a finely divided state prior to coating and, if necessary, can be milled by suitable means to achieve such a state.

In the polymerisation the dispersed inorganic powder particles have a cationic charge on their surfaces. Usually the inorganic powder will require actual treatment with a suitable compound to produce such a cationic charge but in some types of powders a cationic charge can be produced by lowering the pH of an aqueous dispersion of the powder to a value below pH 7 by adding an acid. However for many of the inorganic powders actual treatment with a surface charge modifying agent is necessary.

Typically a dispersion of the inorganic powder is treated with a suitable cation and examples of such cations are Al^{3+}, Zn^{2+}, Th^{4+}, UO_2^{2+} and Pd^{2+}. However the use of aluminium salts is preferred in view of their cost and the size of the ion which is small. Preferably the surface charge modifying agent is an aluminium salt of a mineral acid such as aluminium sulphate or aluminium chloride but most preferably the salt is aluminium nitrate. If desired the inorganic surface charge modifying agent can be replaced in part or supplemented by the use of an organic compound which is cationic in the particular dispersion. If desired the organic compound, itself, can be a polymerisable monomer but non-polymerisable cationic compounds can be used. Preferably the organic compound is a polyelectrolyte and suitable compounds are protein colloids, cationic guar gum, certain polymers of methacrylates, vinyl amine and vinyl

pyridine. Methacrylic acid can be added to the powder dispersion, usually prior to the surface modifying agent as an adjunct, if desired.

The amount of the surface charge modifying agent need only be sufficient to achieve the desired cationic charge density and can be determined easily by electrophoretic or other means. Typical amounts of the surface charge modifying agent will be from 2.5% to 7.5% by weight, of say, an aluminium salt, on weight of inorganic powder depending on the particular inorganic powder to be treated and on the desired cationic charge.

As described the process of the present invention polymerises an ethylenically unsaturated monomer in the presence of a dye to coat the inorganic powder particles with a polymer or copolymer as is desired which contains the dye. Any ethylenically unsaturated monomer which is polymerisable in an emulsion polymerisation system can be used in the present invention. The polymer produced is desirably insoluble in water and, if necessary, may be cross-linked by a suitable cross-linking agent. Typical ethylenically unsaturated monomers are aliphatic or aromatic compounds containing a polymerisable unsaturated group such as the unsaturated carboxylic acids or unsaturated carboxylic acid esters. One of the carbon atoms forming the double bond preferably carries two hydrogen atoms and such compounds can be called vinyl monomers. Typical monomers useful are acidic monomers such as acrylic acid, methacrylic acid, itaconic acid, maleic acid or its anhydride, fumaric acid, crotonic acid. Esters of acid monomers can be used such as methyl acrylate, ethyl

acrylate, methyl methacrylate, butyl acrylate and ethyl methacrylate. Other monomers which can be polymerised to form coatings are styrene, alpha methylstyrene, ethylene, vinyl acetate, vinyl chloride, acrylonitrile, and fluorinated monomers such as fluorinated alkenes, fluorinated acrylic and methacrylic acids and esters and fluorinated ethers.

The monomer used can be selected to produce a polymer which will interact with and bind the dye. For example polymers formed from monomers containing amine groups such as dimethylaminoethyl methacrylate are useful in conjunction with acidic dyes whereas an acidic monomer such as a methacrylate ester produces a polymer more suitable for use with basic dyes.

If desired two or more of the polymerisable monomers can be co-polymerised. Also a cross-linking agent can be present and typical agents are di- or poly-functional ethylenically unsaturated monomers, for example ethylene glycol dimethacrylate, ethylene glycol diacrylate, allyl methacrylate, allyl acrylate, 1,3-butanediol diacrylate, divinyl benzene or 1,3-butanediol dimethacrylate. The amount of such cross-linking agent can be within the range of 10% to 50% by weight of said agent on weight of total monomer employed.

As described hereinbefore the amount of said polymerisable ethylenically unsaturated monomer is not greater than 200% by weight of the inorganic powder and preferably the amount is not greater than 100% by weight. In the most desirable process the

amount of said polymerisable ethylenically unsaturated monomer is within the range 2% to 25% by weight of the inorganic powder.

Any dye can be used in the process of the invention the choice of dye being strongly influenced by the desired colouring effect in the final coated pigment. It is preferable that the dye is soluble in organic media since this enables it to be added as a mixture with one or more of the monomers. When a water soluble dye is used there is a tendency for the dye to be leached into the aqueous phase during the polymerisation but the use of a monomer which interacts with the dye as discussed above restricts loss of dye by this means.

The amount of dye used will depend upon which dye is employed and the effect which it is desired to achieve. However, satisfactory coloured pigments have been produced using between 0.01 and 0.1 grams of dye per gram of inorganic powder.

The inorganic powder usually will be formed into an aqueous dispersion initially, if necessary, with the aid of a dispersing agent. This dispersion can be milled, if desired, and then to the dispersion there is added any necessary surface-modifying agent, followed by, or preceded by, any desired organic polyelectrolyte or other adjunct. When the adjunct is an organic acid such as methacrylic acid an amount of a cross-linking agent such as ethylene glycol dimethacrylate can also be added.

In the process of the invention the chosen monomer usually, prior to mixing with the inorganic powder, is formed into an aqueous emulsion employing, as is necessary, a nonionic or anionic emulsifier

or a mixture thereof to assist the emulsification. Typical emulsifying agents are sodium dodecyl benzene sulphonate and ethoxylated alkyl phenols such as those in which the alkyl group is a nonyl, octyl or decyl group. Other known emulsifying agents can be employed.

Preferably the dye is also formed into an aqueous emulsion together with the chosen monomer but, if desired, can be added separately from the monomer.

Where the polymerisation is to be effected in the presence of a cross-linking agent for the chosen ethylenically unsaturated monomer or monomers then this usually but not always will be added to the inorganic powder separately from the emulsion of the monomer.

Usually the polymerisation is initiated with a water-soluble initiator such as a peroxy compound, a persulphate, a peracetate or a redox initiator, e.g. a salt of a persulphuric acid or an organic hydroperoxide or peroxide in combination with a sulphite, bisulphite, hydrosulphite or metal formaldehyde sulphoxylate. The initiator is added at any suitable stage, e.g. prior to the addition of the monomer to the inorganic powder. Only a part of the required amount of the initiator can be added initially followed by the remaining necessary amount or amounts at one or more later stages.

Alternatively the polymerisation may be initiated by exposing the reaction mixture to a source of gamma radiation such as a Cobalt-60 source.

The polymerisation of the added monomers is usually carried out at an elevated temperature, and depending on the ambient

temperature within the range 25°C to 80°C, usually from 30°C to 50°C. The polymerisation normally but not always is effected in an inert atmosphere, for example, under a protective atmosphere of an inert gas, e.g. nitrogen.

It is important to have efficient agitation during the whole polymerisation since this enables a homogeneous coating layer to be produced. The agitation may be achieved mechanically but a particularly preferred method of agitating the reaction mixture is to use ultrasound for at least part of the polymerisation. The use of ultrasonic vibrations produces a more uniform coating insofar as the degree of coverage is concerned.

The coloured inorganic pigments produced by the process of the invention can be used as opacifiers and colouring agents in paints and other media such as inks. The combination of the opacifying effect of the inorganic powder and the colouring effect of the dye produces desirable optical properties for the pigmented medium.

The invention is illustrated in the following Example.

EXAMPLE

In a glass flask a slurry was produced by mixing 375g of uncoated rutile titanium dioxide produced by oxidation of titanium tetrachloride in a fluid bed reactor and milled in a sand mill and 1.5 l of deionised water purged with nitrogen. 11.25g of methacrylic acid was added to this slurry with mixing and the mixing was continued for 15 minutes. 16.88g aluminium nitrate was then added and the slurry stirred for a further 15 minutes after which 5.62g ethylene

dimethacrylate was added and the mixture was heated to 40°C. A mixture of 3.60g of a 1% aqueous solution of potassium persulphate and 1.80g of a 1% aqueous solution of sodium metabisulphite was added and the mixture stirred for 15 minutes. An emulsion was prepared from 150.0g of demineralised water, 45.0g methyl methacrylate, 4.5g of an emulsifying agent sold under the Trade Name of "Triton-X" and 18.75g of one of the dyes listed in Table 1 below. This emulsion was then added to the reaction mixture over 15 minutes followed immediately by 16.2g of ethylene glycol dimethacrylate. The slurry was heated to 70°C and a mixture of 14.4g of a 1% aqueous solution of potassium persulphate and 7.2g of a 1% aqueous solution of sodium metabisulphite was added. The stirred reaction mixture was maintained at 70°C for 4 hours then cooled and filtered to separate a coloured pigment as indicated below in Table 1. The pigment produced was washed thoroughly and dried.

TABLE 1

Dye		Pigment Colour
Trade Name	Description	
Orasol Yellow 2RN	Cobalt complex	Yellow
Orasol Red G	Cobalt complex	Red
Fluorol Yellow 086	Nonionic polycyclic	Yellow
Irgalite Yellow CG	Diazo Arylamide (CI Pigment Yellow 16)	Yellow

CLAIMS

1. A process for the preparation of coloured inorganic pigments comprising polymerising an ethylenically unsaturated monomer in the presence of a dye and of a dispersed inorganic powder having a cationic charge on the surface of the particles thereof, said monomer being present in an amount not greater than 200% of the weight of said powder so that said particles are coated with polymerised monomer containing said dye.

2. A process according to claim 1 in which the inorganic powder is an inorganic pigment, extender or filler.

3. A process according to claim 2 in which the inorganic pigment is titanium dioxide pigment.

4. A process according to any one of the preceding claims in which the cationic charge is produced on the inorganic powder by reducing the pH of an aqueous dispersion of the powder below 7 by addition of an acid.

5. A process according to any one of claims 1 to 3 in which the cationic charge is produced by treatment of the inorganic powder with a surface charge modifying agent.

6. A process according to claim 5 in which the surface charge modifying agent is an aluminium salt of a mineral acid.

7. A process according to claim 6 in which the amount of aluminium salt used is from 2.5 to 7.5% by weight based on weight of inorganic powder.

8. A process according to claim 5 or 6 in which a cationic organic compound is used as a surface charge modifying agent.

9. A process according to any one of the preceding claims in which the ethylenically unsaturated monomer is an unsaturated carboxylic acid or an unsaturated carboxylic acid ester.

10. A process according to any one of the preceding claims in which the ethylenically unsaturated monomer is a vinyl monomer.

11. A process according to any one of the preceding claims in which the ethylenically unsaturated monomer is a fluorinated monomer.

12. A process according to any one of the preceding claims in which the ethylenically unsaturated monomer produces a polymer which interacts with and binds the dye.

13. A process according to any one of the preceding claims in which a plurality of ethylenically unsaturated monomers is used.

14. A process according to any one of the preceding claims in which a cross-linking agent for said polymerised monomer is present.

15. A process according to claim 14 in which the cross-linking agent is ethylene glycol dimethacrylate, ethylene glycol diacrylate, allyl methacrylate, allyl acrylate, 1,3-butanediol diacrylate, 1,3-butanediol dimethacrylate or divinyl benzene.

16. A process according to claim 14 or 15 in which the amount of cross-linking agent is within the range of 10% to 50% by weight of said agent on weight of total monomer employed.

17. A process according to any one of the preceding claims in which the amount of ethylenically unsaturated monomer employed is not greater than 100% by weight of said powder.

18. A process according to claim 17 in which the amount of ethylenically unsaturated monomer employed is within the range 2% to 25% by weight of the inorganic powder.

19. A process according to any one of the preceding claims in which the amount of dye used is between 0.01 and 0.1g per gram of inorganic powder.

20. A process according to any one of the preceding claims in which the dye and the ethylenically unsaturated monomer are premixed before addition to the dispersed inorganic powder.

21. A process according to any one of the preceding claims in which the dye is present during only part of the polymerisation process.

22. A process according to any one of the preceding claims in which the inorganic powder is milled before coating with the polymerised monomer.

23. A process according to any one of the preceding claims in which the inorganic powder is dispersed with the aid of a dispersing agent.

24. A process according to any one of the preceding claims in which the ethylenically unsaturated monomer is formed into an aqueous emulsion prior to mixing with the inorganic powder.

25. A process according to claim 24 in which formation of the aqueous emulsion is assisted by employing a nonionic or anionic emulsifier.

26. A process according to claim 25 in which the emulsifier is sodium dodecyl benzene sulphonate or an ethoxylated alkyl phenol in which the alkyl group is an octyl, nonyl or decyl group.

27. A process according to any one of the preceding claims in which the polymerisation is initiated with a water-soluble peroxy compound, persulphate, peracetate or a redox initiator.

28. A process according to any one of claims 1 to 26 in which the polymerisation is initiated by exposing the ethylenically unsaturated monomer to a source of gamma radiation.

29. A process according to any one of the preceding claims in which the polymerisation is carried out at a temperature within the range 25°C to 80°C.

30. A process according to claim 29 in which the temperature is within the range 30°C to 50°C.

31. A process according to any one of the preceding claims in which the polymerisation is carried out under an atmosphere of inert gas.

32. A process according to any one of the preceding claims in which the mixture of ethylenically unsaturated monomer and inorganic powder is agitated by the use of ultrasound during at least a part of the polymerisation.

33. A coloured inorganic pigment when prepared by a process according to any one of claims 1 to 32.

34. A process for the preparation of coloured inorganic pigments substantially as described herein with reference to the Example.

Pat nts Act 1977
Examiner's report to th Comptroller under ection 17 (The Search Report)

Application number
9025667.8

Relevant Technical fields

(i) UK Cl (Edition K) C1A:AVF1,AVF3

(ii) Int Cl (Edition 5) C09C

Search Examiner
B S STRINGER

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASES:WPI AND CLAIMS

Date of Search
30 JANUARY 1992

Documents considered relevant following a search in respect of claims 1-34

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
Y	GB 2227739 A (TIOXIDE) see especially Claim 1 and examples	1
Y	HU T35709 A (ATTILA TUDOMANYEGYE) see English Abstract	1

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).

Published 1992 at The Patent Office, Concept House, Cardiff Road, Newport, Gwent NP9 1RH. Further copies may be obtained from Sales Branch, Unit 6, Nine Mile Point, Cwmfelinfach, Cross Keys, Newport, NP1 7HZ. Printed by Multiplex techniques ltd, St Mary Cray, Kent.